ADHESIVE BONDING OF CARBON FIBER REINFORCED PLASTIC TO ADVANCED HIGH STRENGTH STEEL

YONG CHAE LIM, JIAN CHEN, HUI HUANG, DAVID WARREN, ZHILI FENG (PI)

OAK RIDGE NATIONAL LABORATORY

KEVIN SIMMONS (CO-PI), YONGSOON SHIN, GAYANEH PETROSSAN, ANGEL ORTIZ, LEO FIFIELD

PACIFIC NORTHWEST NATIONAL LABORATORY

2020 DOE VTO ANNUAL MERIT REVIEW

JUNE 02, 2020

Project ID # MAT-137

Pacific Northwest NATIONAL LABORATORY

OAK RIDGE National Laboratory

OVERVIEW

Timeline

- Start: Oct, 2017
- Finish: Sept, 2020
- 70% Complete

Budget

- Project Funding – $1.867M
  - FY18 - $667K
  - FY19 - $600K
  - FY20 - $600K

Barriers

- Limited scientific understanding of bonding mechanisms for metal to composite joints
- Few technologies exist for joining metals to composites and limited by:
  - Low joint strength
  - Crack arrest resistance in crash
  - Thermal expansion mismatch
  - Durability and environmental effects

Partners

- Oak Ridge National Laboratory
- Pacific Northwest National Laboratory

RELEVANCE

- **EERE-VTO Goal:**
  - By 2025, demonstrate a cost-effective 25% weight reduction in passenger vehicles compared to 2010 model baseline (2017 U.S. DRIVE Roadmap Report, Section 5)
  - **This research aims to enable increased use of CFRP in multi-material body structure for weight reduction**

- **Project Objectives**
  - Focuses on the fundamentals of adhesive bonding of carbon fiber reinforced polymer (CFRP) to advanced high strength steel (AHSS). In concert with the Interface by Design (IFBD) effort, innovative adhesive bonding concepts are being identified and explored
  - The goal is to significantly improve the performance and productivity of adhesive bonding in high volume auto body assembly, and to develop better tools for adhesive performance, joint design, and lifetime prediction

FY20 MILESTONES

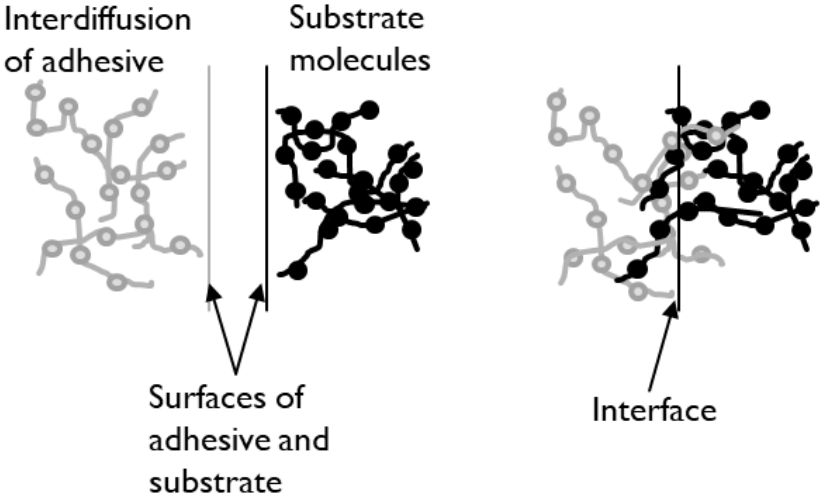
Milestone Name/Description	End Date	Type
Demonstrate surface modifications, including plasma, hot gas and transfer films on CFRP, and chemical treatments on adherends to show increased surface chemistry functionality by changing surface energy for improve bonding strength of thermoplastic CFRP to bare steel	12/30/2019 Completed	Quarterly Progress Measure (Regular)
Assessment of TRL of the task and develop plan for targeted development and for tech transition in FY21 & 22	9/30/2020	Quarterly Progress Measure (Regular)

APPROACH

ADDRESSING TWO FUNDAMENTAL ASPECTS OF ADHESIVE ADHESION/BONDING PHENOMENA

Chemical

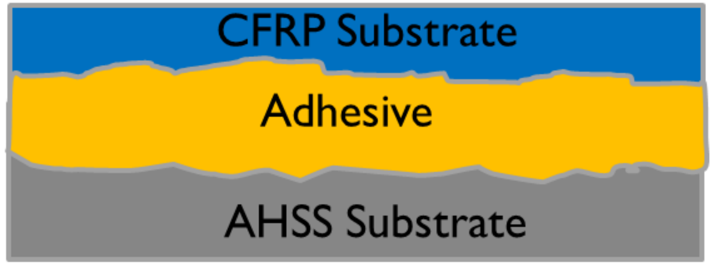
- ❖ Intrinsic Adhesion - referring to the direct molecular forces of attraction between the adhesive and the substrates
  - ◆ Surface Tension - interatomic and intermolecular forces

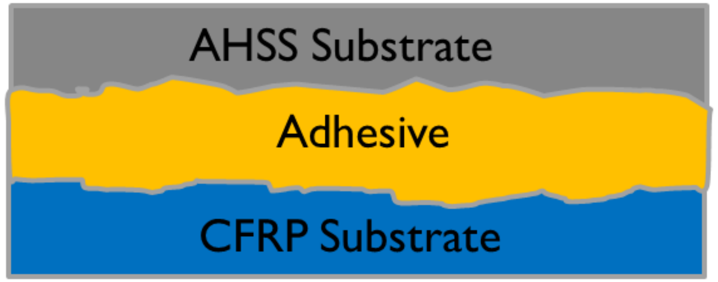


Physical

- ❖ Measured Adhesion - measured strength or toughness of an adhesive joint
  - ◆ Surface Roughness – Effective adhesion area

Surface Roughness for Mechanical Interlocking



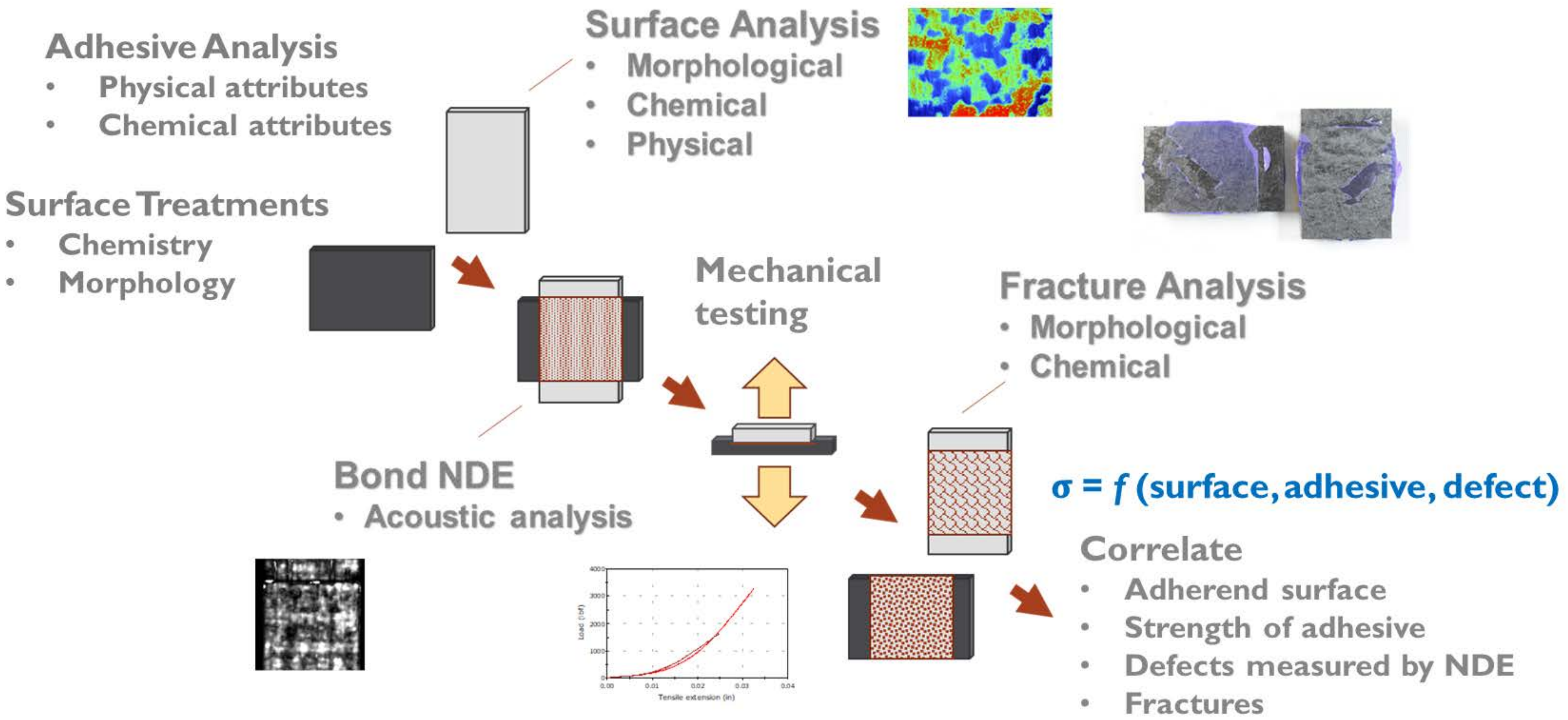


Good Wetting

Poor Wetting

APPROACH

INVESTIGATING THE RELATIONSHIP BETWEEN SURFACES AND ADHESIVES

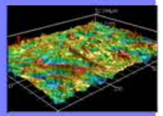


APPROACH

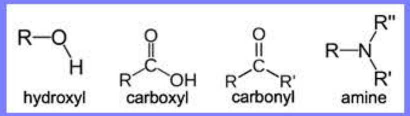
IMPROVE BOND STRENGTH BY TAILORING ADHEREND SURFACE

Activity One

Surface engineering



- PPA resin only, CFRP(PPA), Steel
- Surface morphology: mechanical, laser
- Surface chemistry: plasma, hot gas, transfer film, chemical surface treatment



Activity Two

Evaluating joint performance

- Macroscopic level: lap shear tensile, cross tension pull, double cantilever testing
- Microscopic level: miniature lap shear tensile testing with μ-DIC system
- Environmental testing

Collaboration with IFBD

Characterization

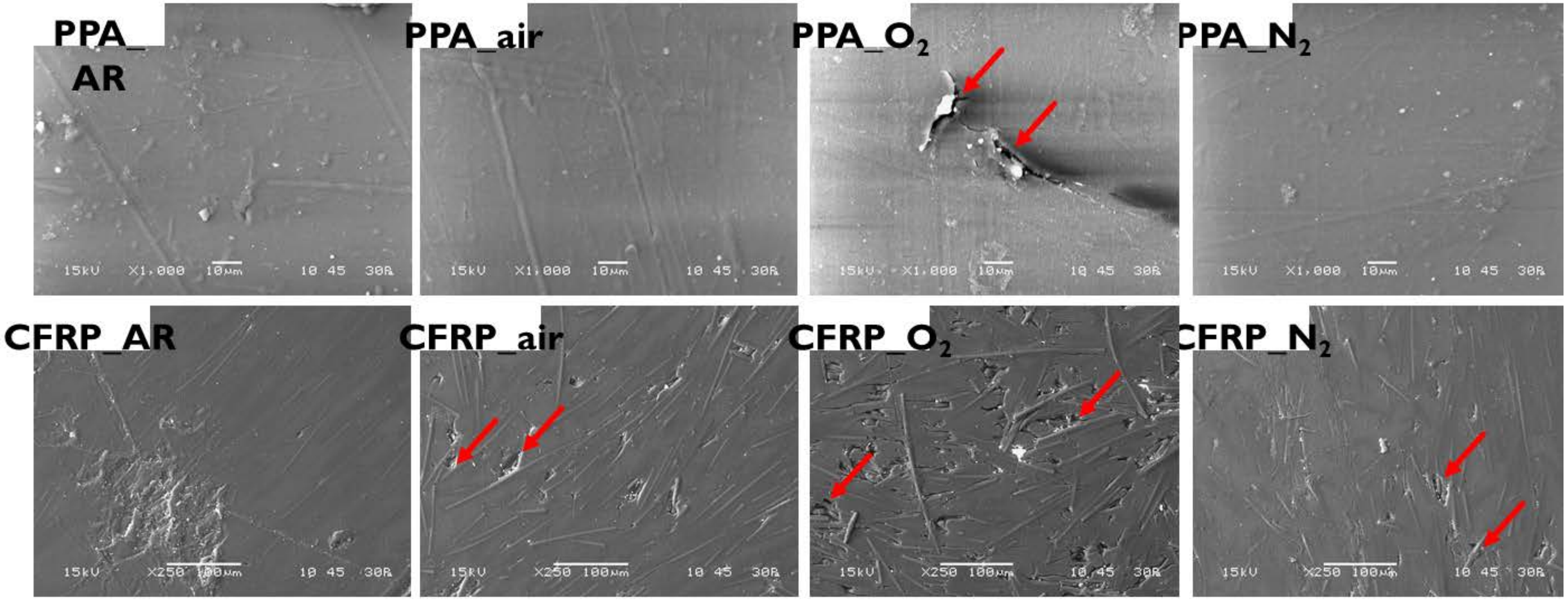
Understand Surface/interface

- Surface energy (contact angle)
- Chemical functional groups by advanced analytical tools (laser confocal profilometry, SEM, FTIR, XPS, TOF-SIMS, etc.)
- Micro/nano scale bond interface characterizations (TEM, nano-indentation)
- Bonding interface deformation and failure by μ-DIC

ACCOMPLISHMENT AND PROGRESS

DIFFERENT PLASMA EFFECTS SURFACE MODIFICATION ON ADHERENDS

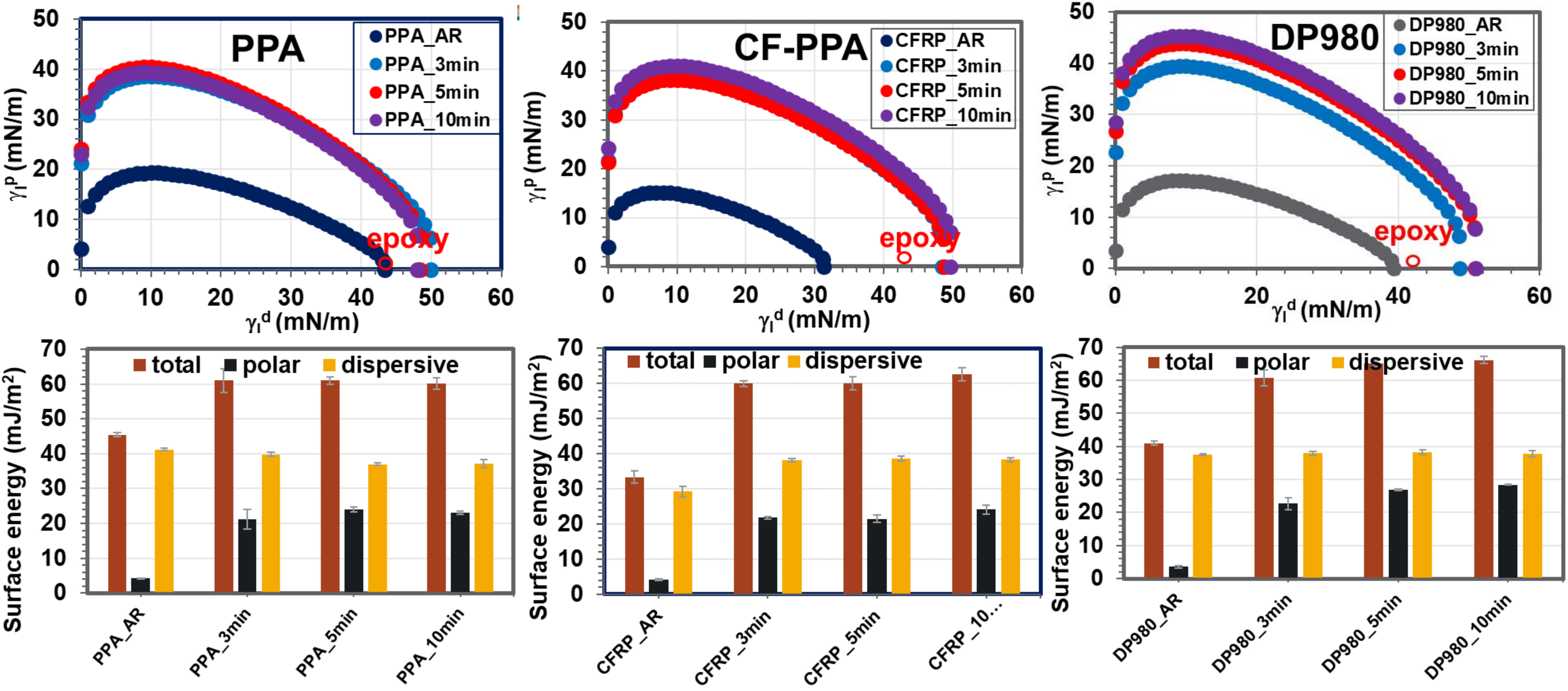
Air and nitrogen surfaces show minimal effects to damaging the surface
Oxygen plasma illustrates extremely small surface crazing around the large surface crack



Carbon fiber influences the plasma on the surface
Small cracks and some erosion shown around the carbon fibers in air and nitrogen
Oxygen plasma treatment shows significant polymer crazing and erosion around carbon fibers
Some polymer completely removed from fiber surfaces after oxygen plasma treatment

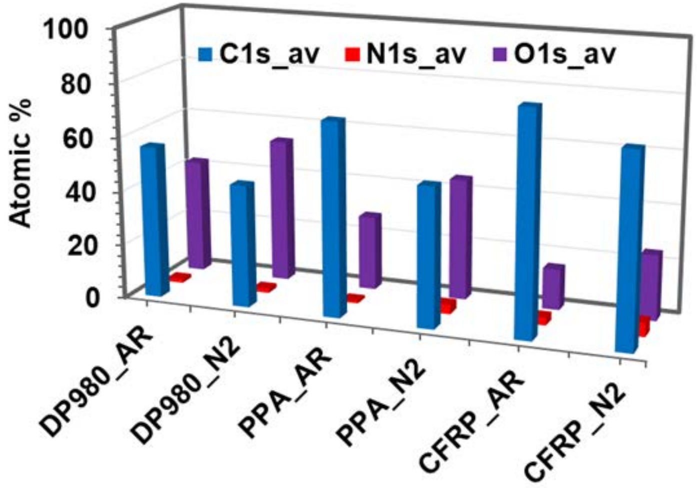
ACCOMPLISHMENT AND PROGRESS

DEVELOPMENT OF WETTABILITY ENVELOPES TO EVALUATE THE EFFECTS OF SURFACE TREATMENTS: N_2 PLASMA SURFACE MODIFICATION ON ADHERENDS



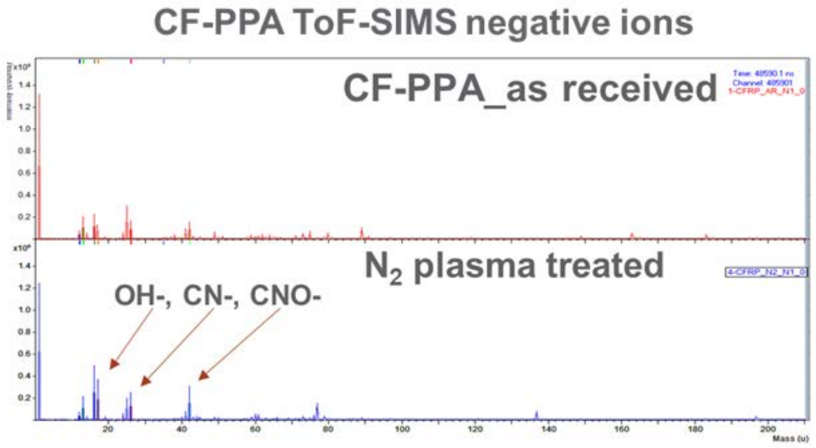
ACCOMPLISHMENT AND PROGRESS

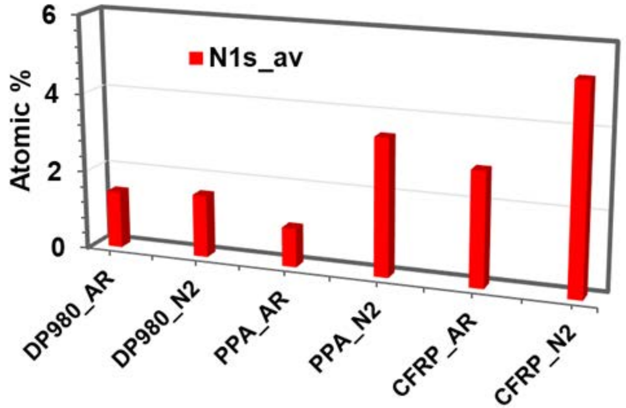
CHEMICAL ANALYSIS ILLUSTRATES CHEMICAL CHANGES ON TREATED ADHEREND SURFACES



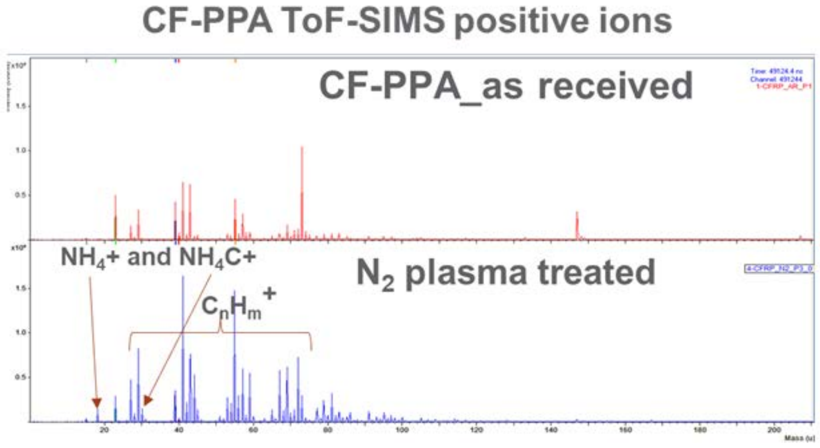
N2 Plasma Treated Surfaces

ToF-SIMS shows an increase of nitrogen element chemistries on PPA resin and CF-PPA after N_2 plasma treatment



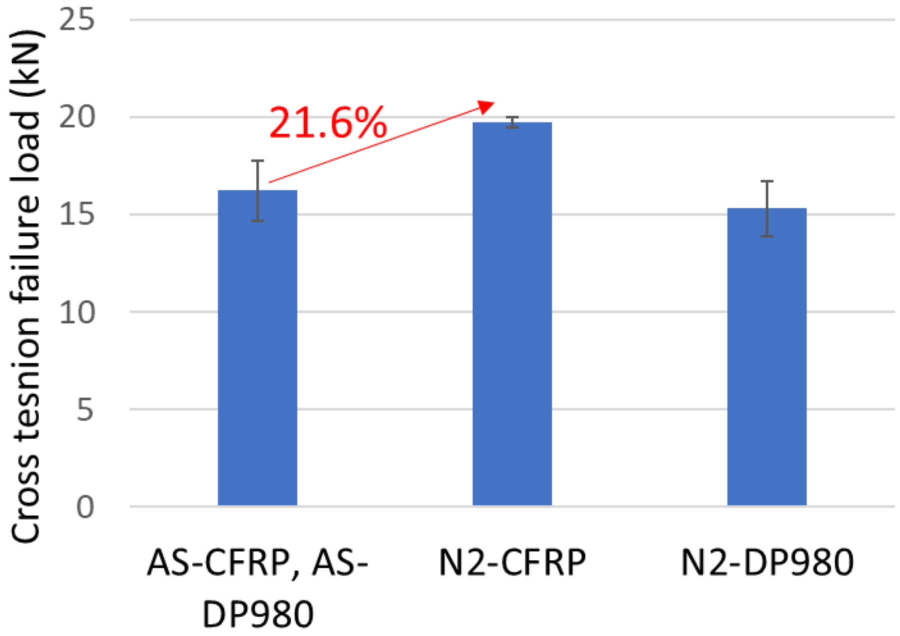


XPS shows an increase of nitrogen element on PPA resin only and CF-PPA after N_2 plasma treatment

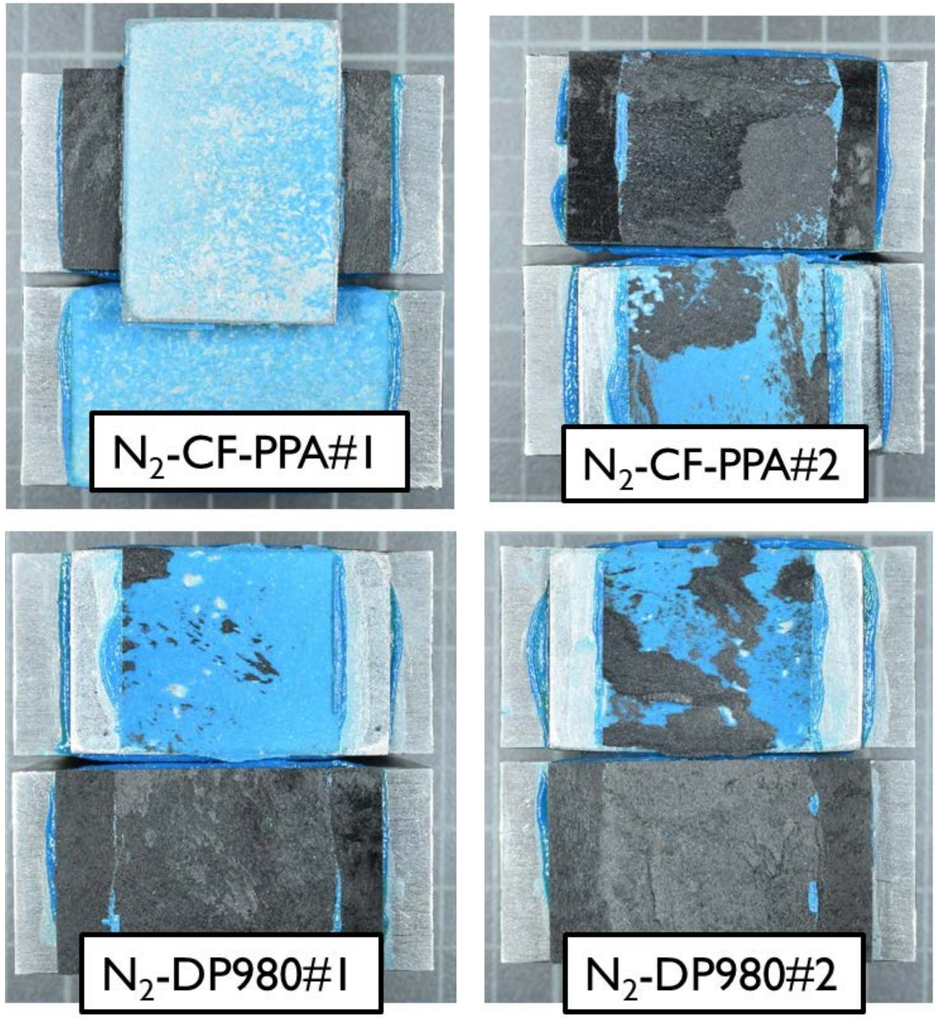


ACCOMPLISHMENT AND PROGRESS

N_2 PLASMA TREAT INCREASED ADHESION IN CROSS TENSION MECHANICAL TESTING

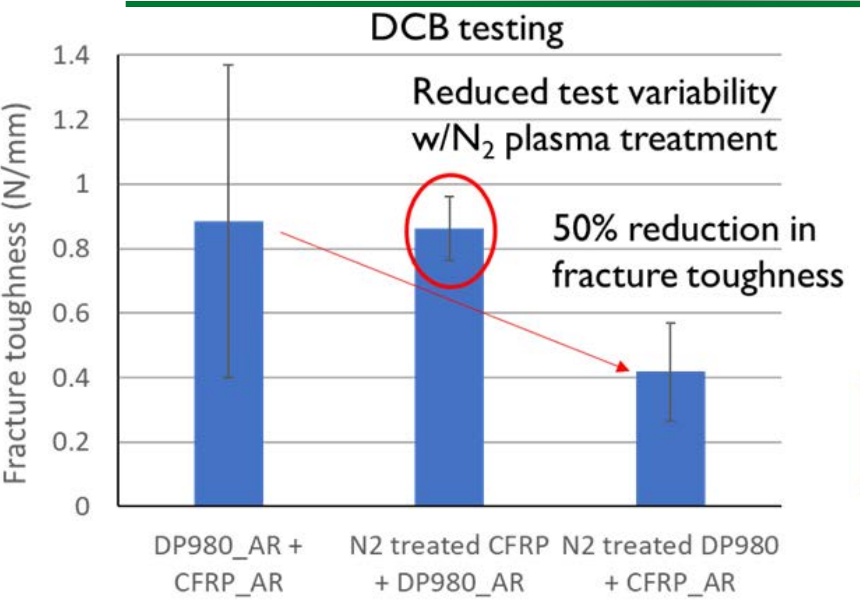


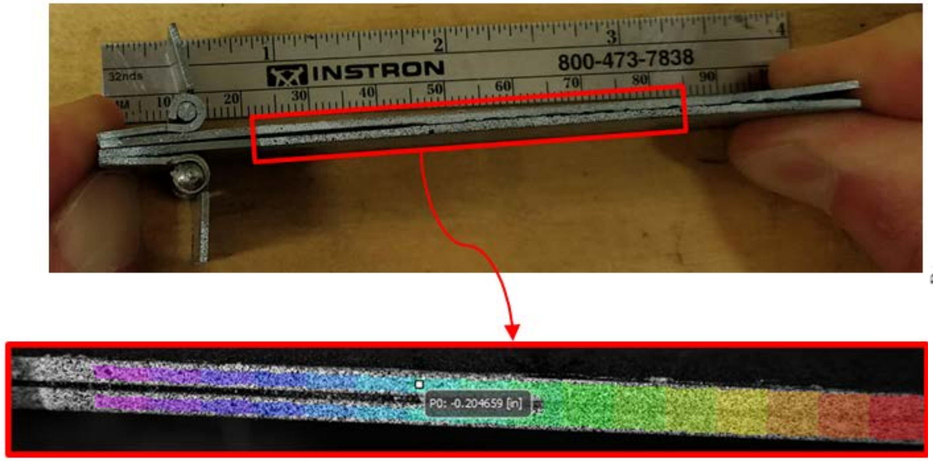
Adhesive Modulus >2000 MPa



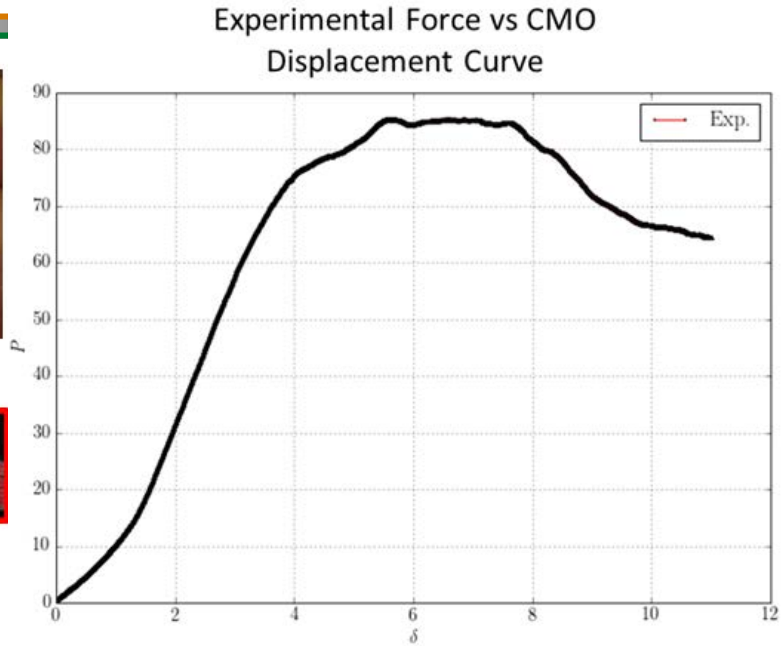
ACCOMPLISHMENT AND PROGRESS

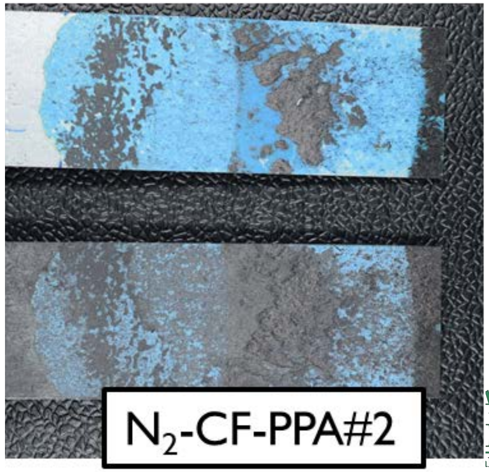
EXPERIMENTAL DATA FOR INTERFACE BY DESIGN MODELS

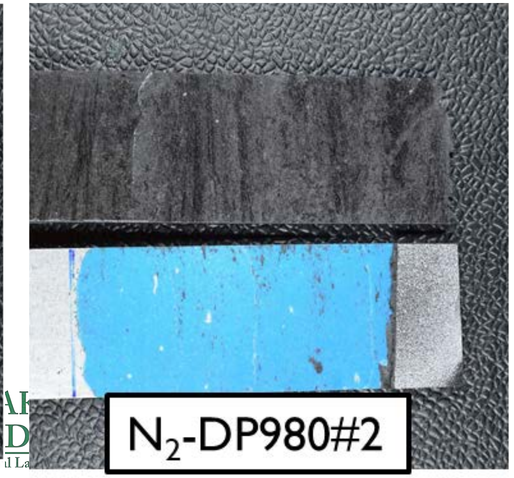




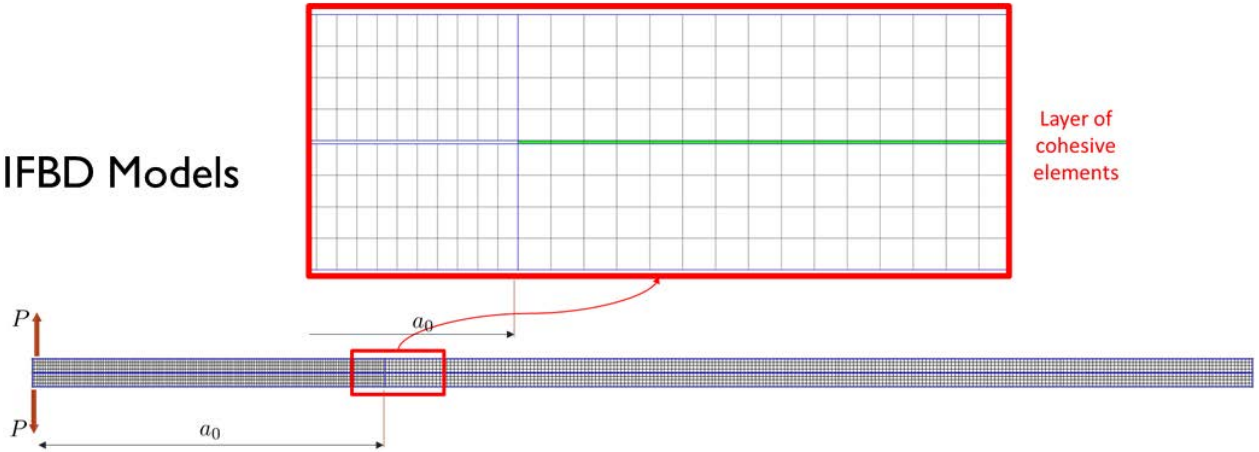
N_2 plasma treated adherends





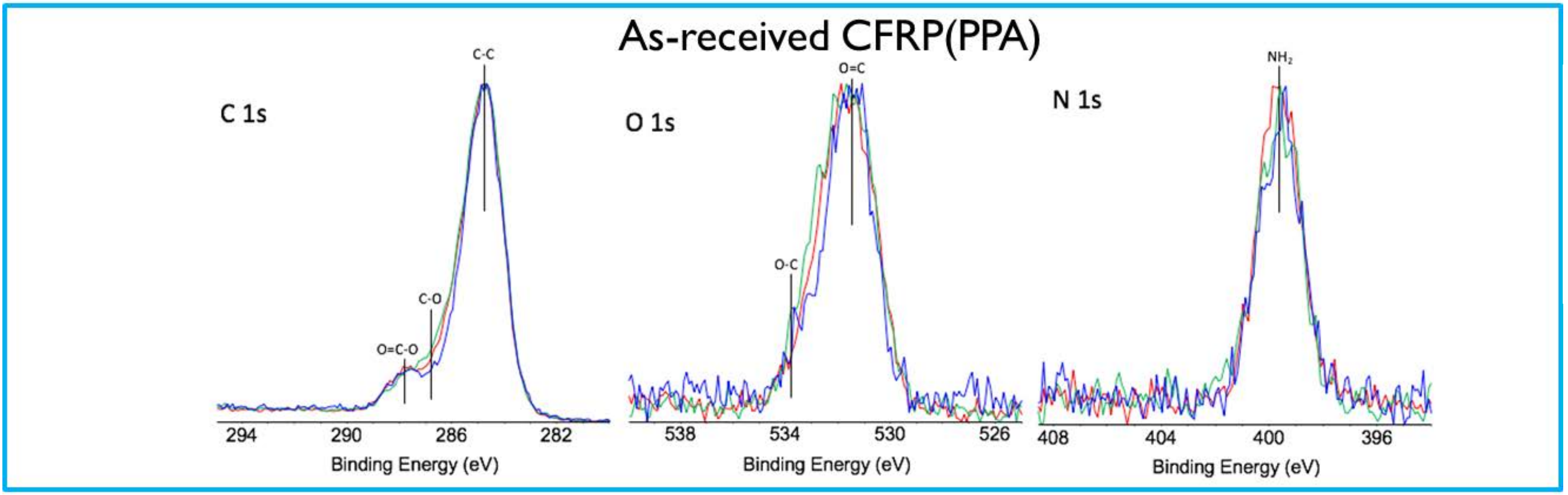


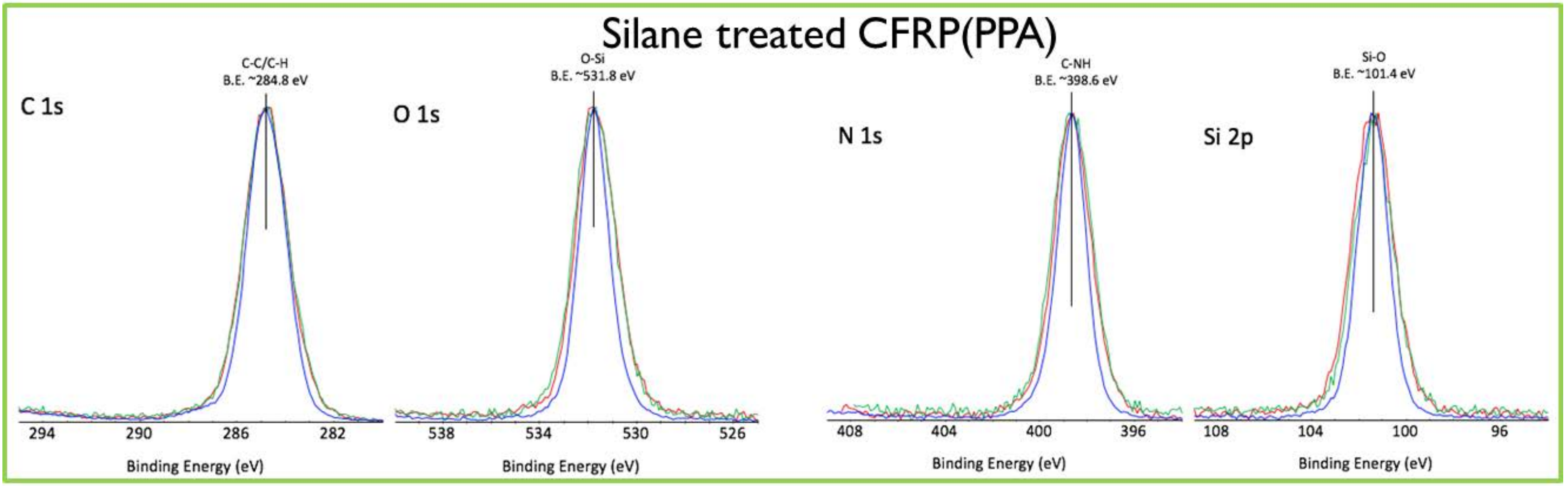
IFBD Models



ACCOMPLISHMENT AND PROGRESS

X-RAY PHOTOELECTRON SPECTROSCOPY REVEALED SURFACE CHEMISTRY CHANGES OF SILANE TREATED CF-PPA





Surface Composition (at.%)

	C	O	N	Si	Ca	Cl	S
A_CFC-1	83.4	9.0	6.5	0.7	0.4	0.1	0.0
A_CFC-2	83.3	8.5	6.0	0.8	0.3	0.2	0.8
A_CFC-3	83.9	7.1	7.7	0.8	0.5	0.0	0.0

Epoxy amine

Surface Composition (at.%)

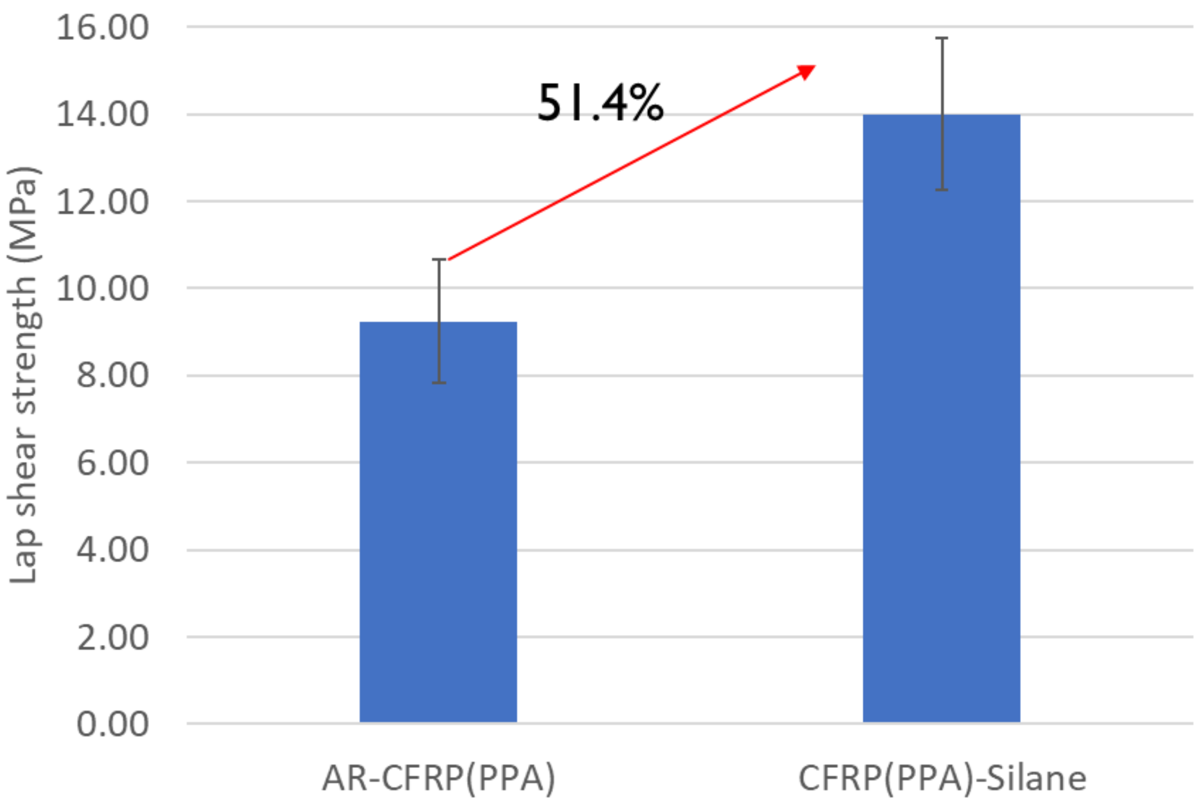
	C	N	O	Si
A_CFRC-1	58.4	16.0	14.7	10.9
A_CFRC-2	57.3	16.3	14.3	12.2
A_CFRC-3	56.8	16.9	15.8	10.4

Silane treatment on CF-PPA increases N, O, and Si element, compared with as-received CF-PPA

ACCOMPLISHMENT AND PROGRESS

OVER 50% IMPROVEMENT IN BONDING STRENGTH BY SILANE TREATED CFRP(PPA)

- Silane contains functional groups that bond with both organic and inorganic materials
- Silane treatment was only applied on as-received CFRP(PPA) prior to adhesive bonding
- Low modulus adhesive was used
- Tensile shear strength for silane treated CF-PPA was increased to 14.0 MPa from 9.25 MPa for as-received CF-PPA



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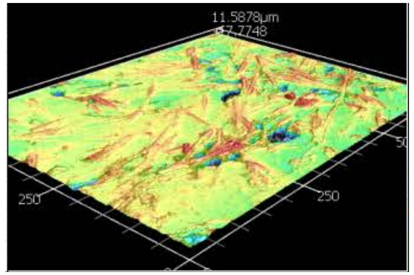
ACCOMPLISHMENTS AND PROGRESS

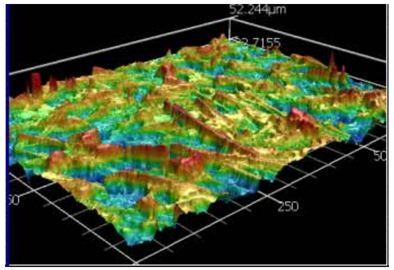
IMPROVEMENT IN BONDING STRENGTH BY LASER TREATMENT ON CFRP(PPA) SURFACE

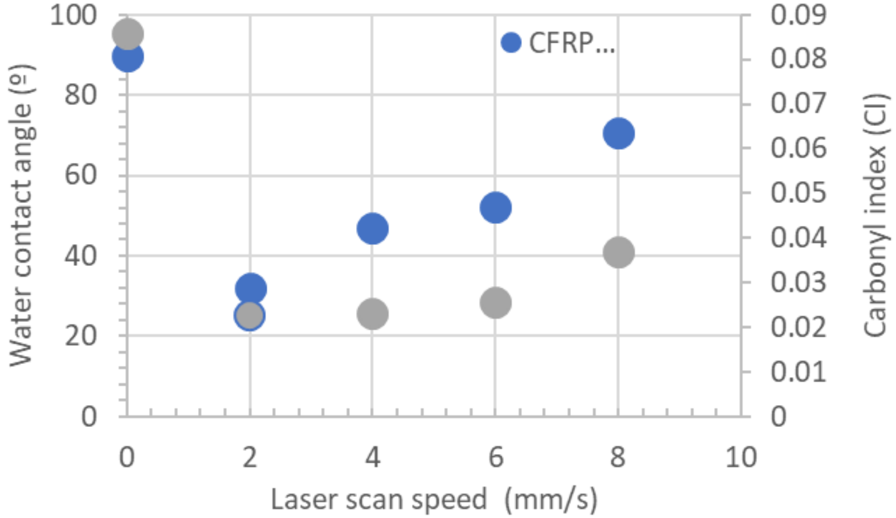
Laser treatment results in changes in both surface roughness and surface energy

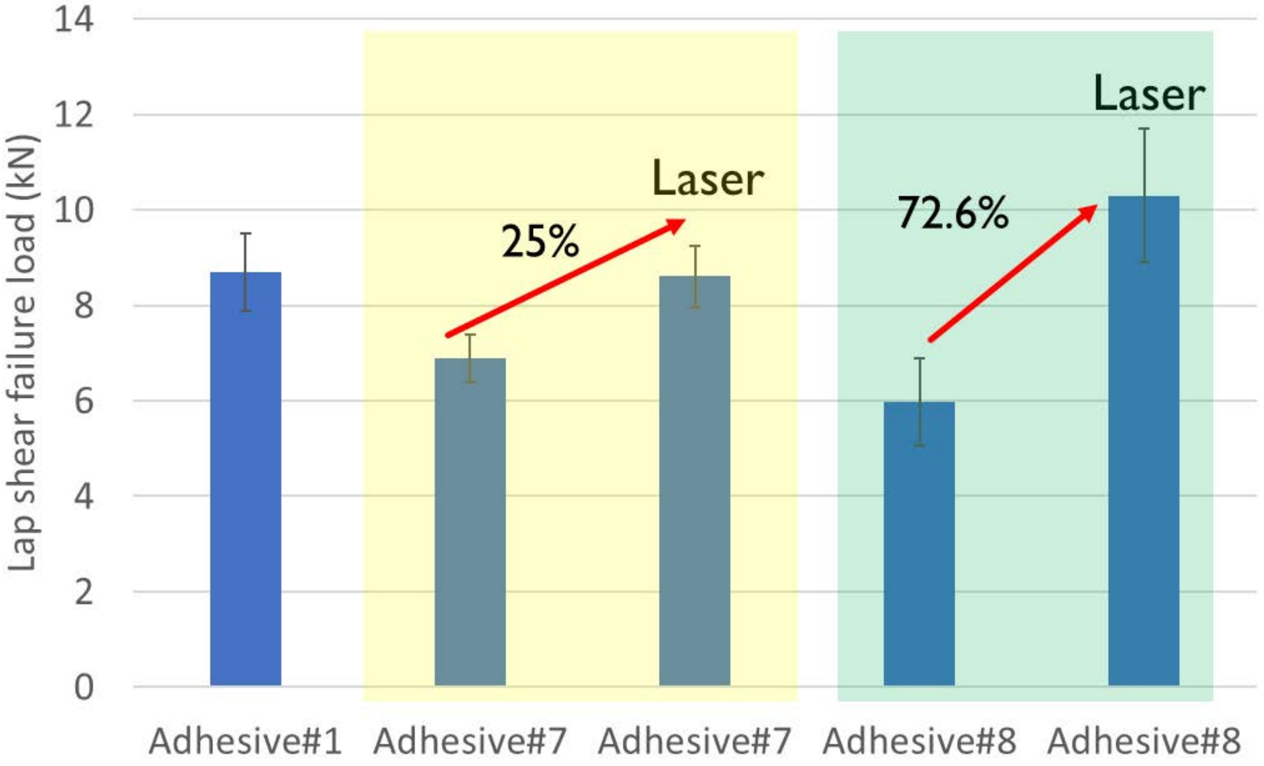
As-received CFRP (PPA)



Laser treated CFRP (PPA)



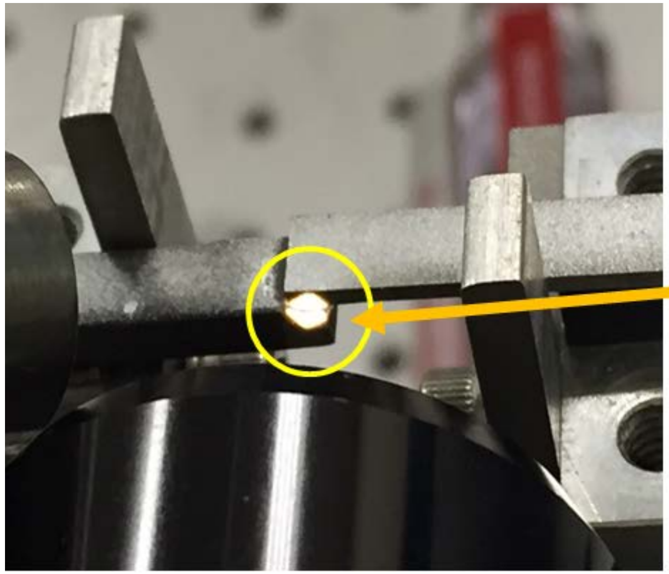




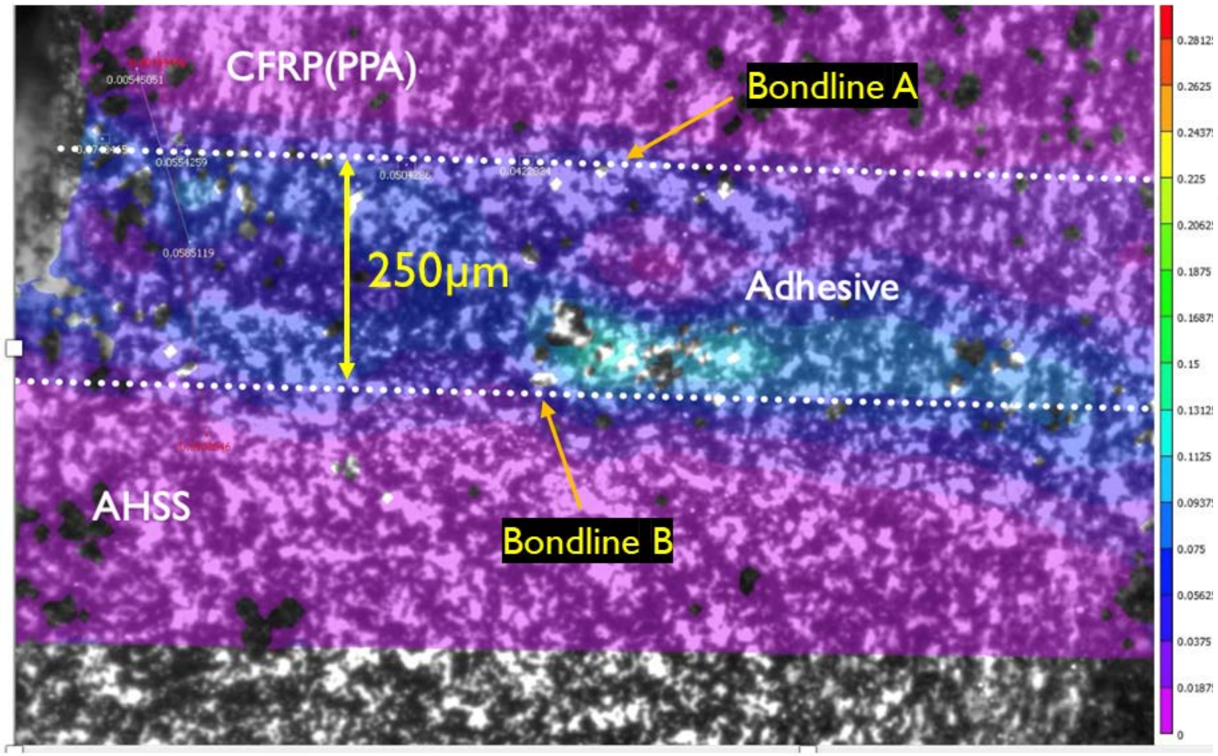
ACCOMPLISHMENT AND PROGRESS

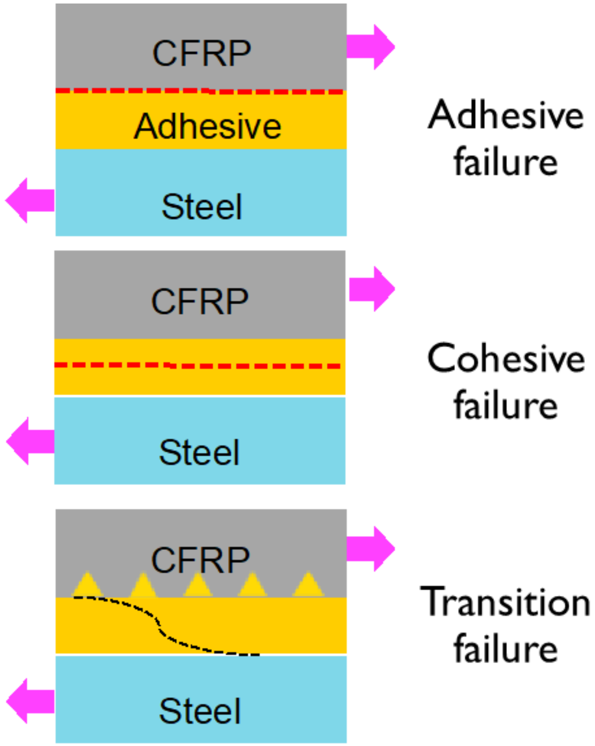
UNDERSTANDING DEFORMATION AND FAILURE OF BONDING INTERFACE

- Developed an in-house test system (μ-DIC) to quantify the microscopic deformation and failure of bonding interface
  - Full field strain mapping covering the entire bonding interface (adhesives, bond-lines, and adherends) as function of applied load.
  - Observation of strain localization, failure progression, and failure location and mode of the bonding interface at micron-level
  - Quantification of critical failure strain values as function of adhesive, surface treatment, adherends, etc …



μ-DIC system





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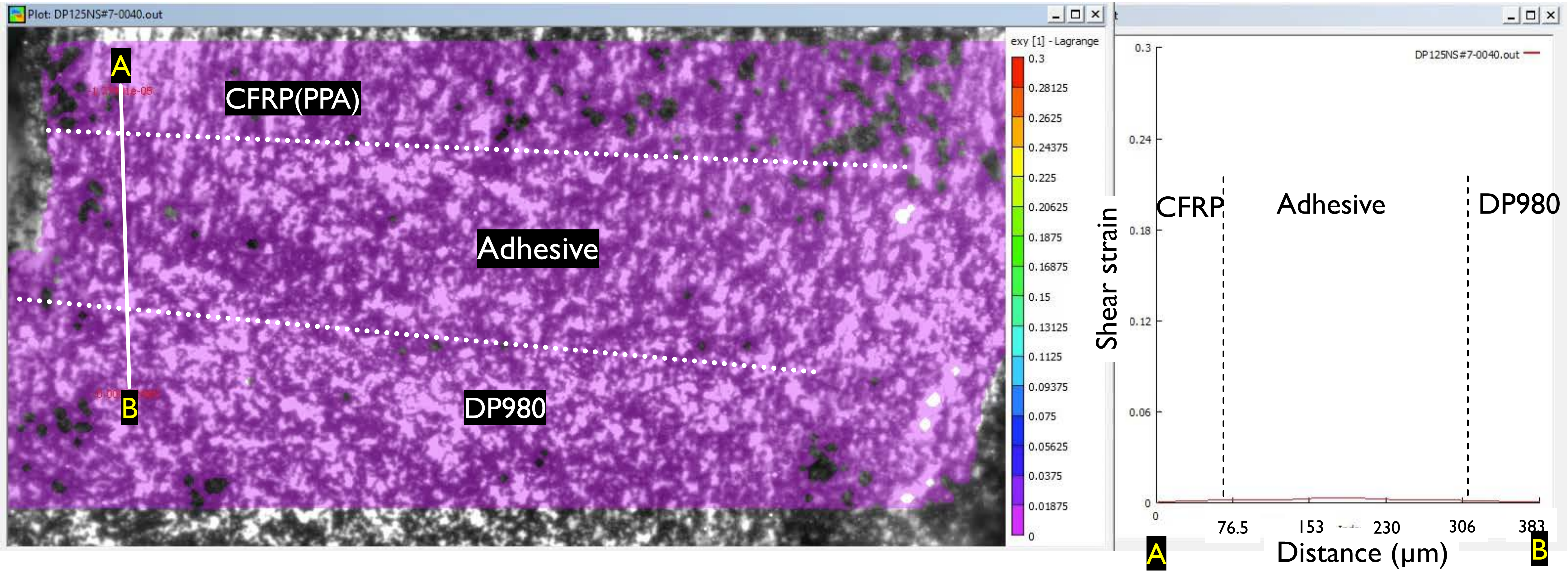
ACCOMPLISHMENT AND PROGRESS

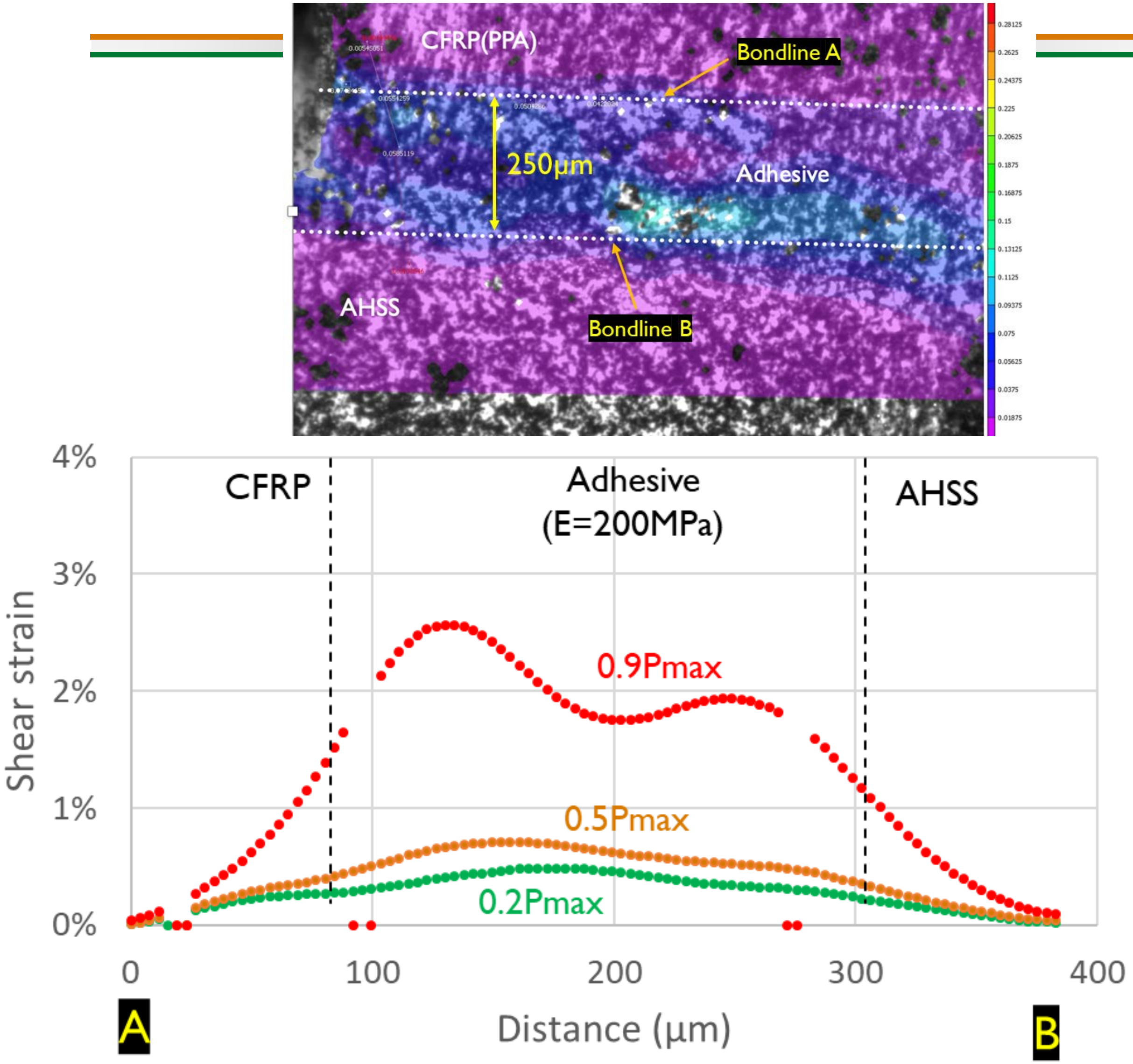
μ-DIC MEASUREMENT OF DEFORMATION AND FAILURE OF BONDING INTERFACE

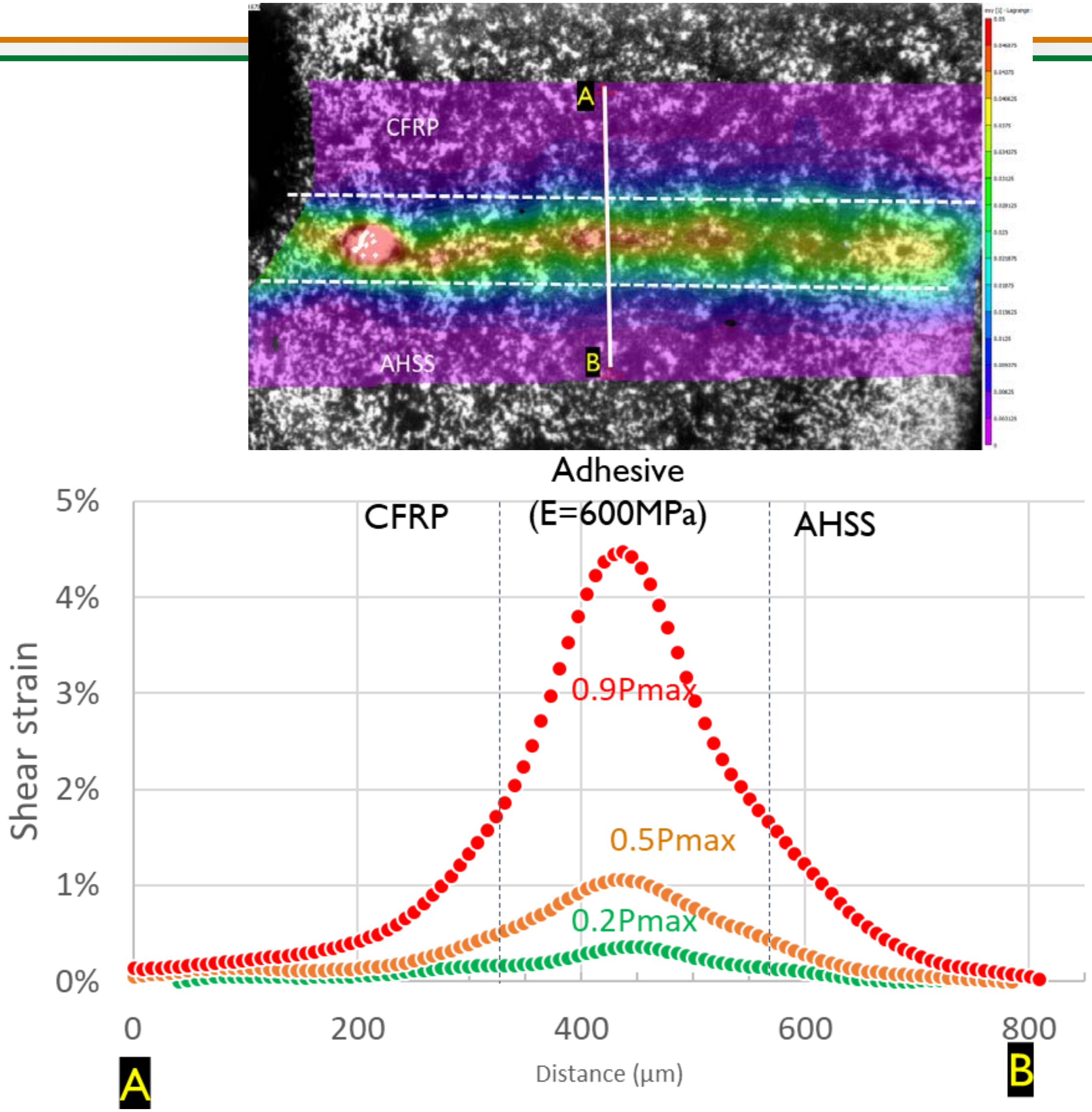


CFRP(PPA), DP980 and low modulus adhesive (~200MPa)

ACCOMPLISHMENT AND PROGRESS

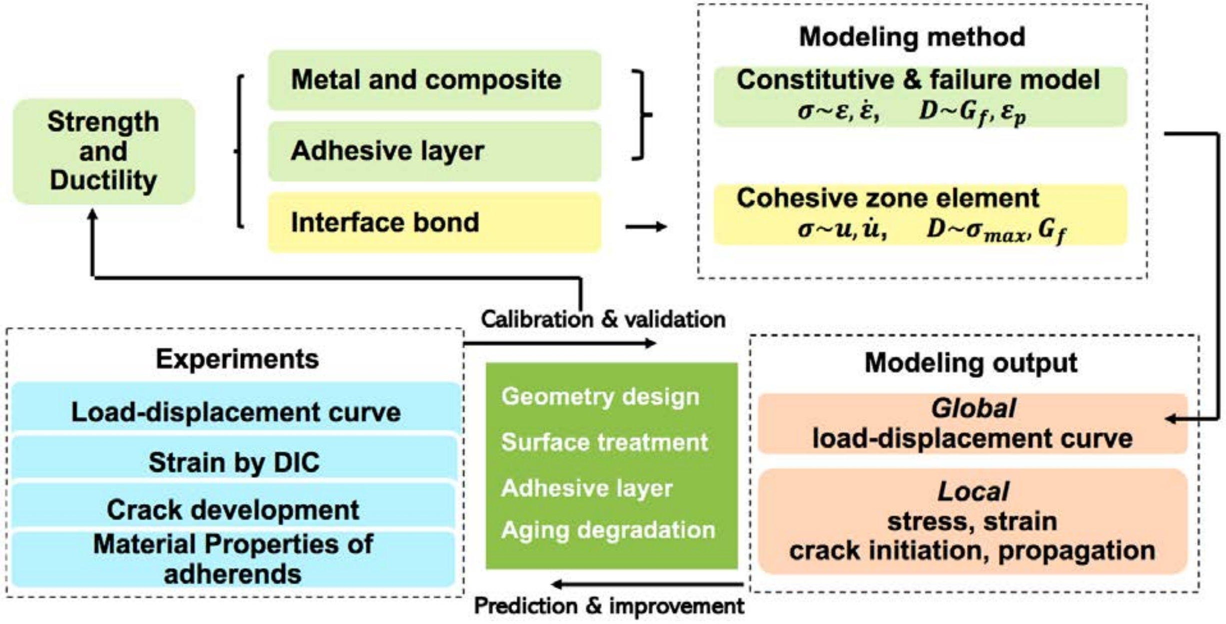
DEFORMATION EVOLUTION OF ADHESIVE BOND INTERFACE REGION

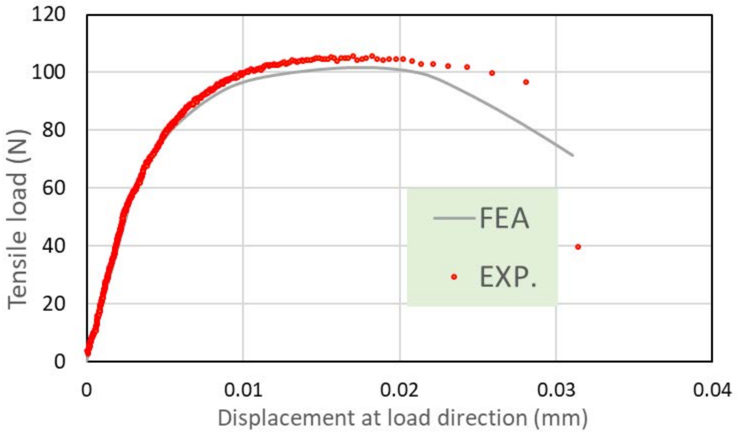


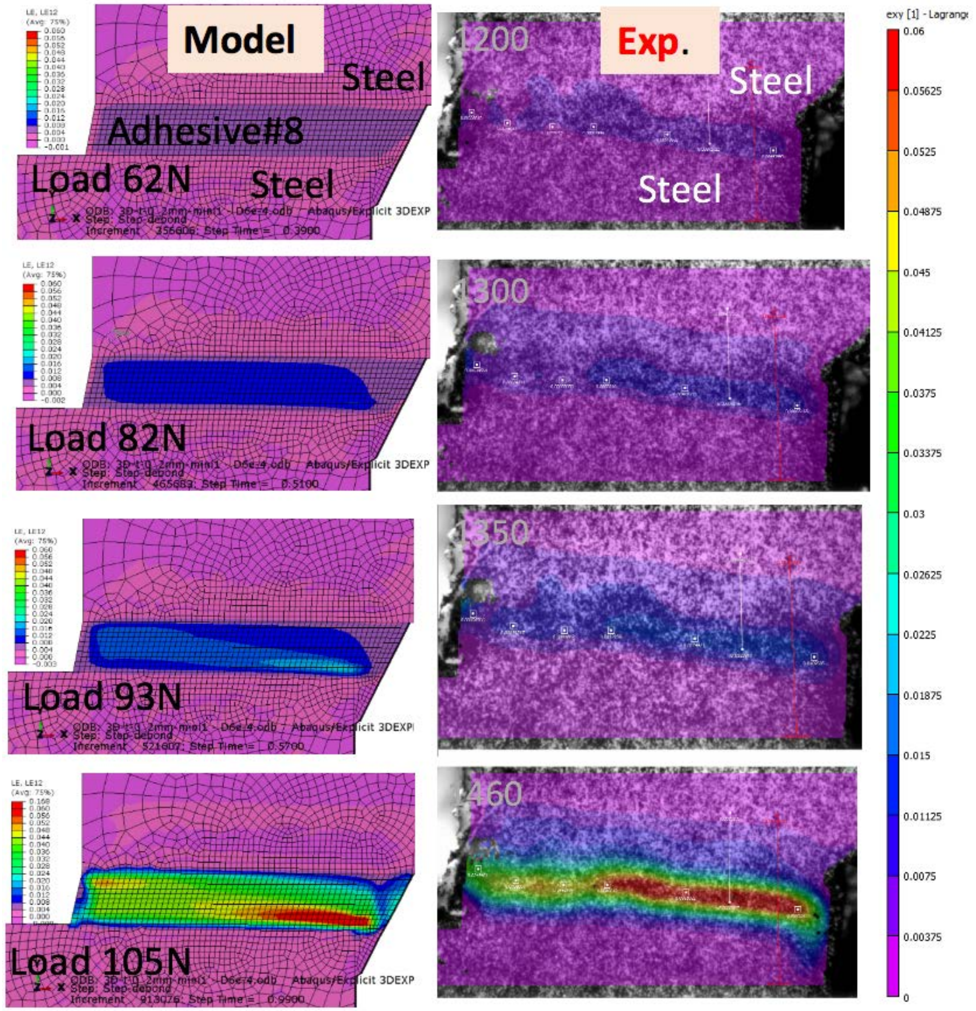


ACCOMPLISHMENT AND PROGRESS

μ-DIC MEASUREMENT SUPPORTS MULTI-SCALE ADHESIVE BOND PREDICTIVE MODEL DEVELOPMENT







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RESPONSES TO PREVIOUS YEARS REVIEWERS' COMMENTS

- *"The reviewer remarked that this program is an important area that has great technical leverage. There are great tools being used and available to the team. … There is not a clear focus on a key scientific or technical question."*
  - **Response:** In FY20, we focused on the understanding of the effects of chemical surface modification on joint strength, and the understanding of micro level interface/adhesive deformation and failure cauterization.
- *"There is already significant work on surface modification processes for adhesive bonding. What is really lacking is a fundamental understanding of what is happening at the adhesive/CFRP interface and how that is affected by environment (moisture), which is critical since industry would typically need to introduce a peel stopper in conjunction with the adhesive."*
  - **Response:** In FY20, we completed the development of a special mechanical testing system with microscopic level DIC (m-DIC). It enabled us to investigative the fundamentals of deformation and failure of adhesives, bond-lines and adjacent substrate material as function of adhesive bonding process, properties of adhesives. We also used different characterization techniques to connect the improvement in bond strength to the surface chemistry and morphology modifications in the study. We will soon begin to investigate the environment effect with the above methods and other tools as needed, including the long-term environmental effects.
- *"The collaboration with the Interface by Design team Is not very clear. Perhaps the scope of the project activities and details affect the collaboration needs, but at the moment the collaboration appeared disjointed and not aligned with the overall project objectives."*
  - **Response:** We began to develop a multi-scale adhesive bond performance model in late part of FY19, under the interface by design task with experimental assistance in this task. This predictive model is promising, and useful in our joint design/surface modification studies.

COLLABORATION AND COORDINATION

- An integrated R&D team from ORNL and PNNL and Industry partners
  - PNNL and ORNL analytical capabilities position the partnership to provide the most advanced characterization suite of constituent components in adhesive joining to support development
  - Closely coordinated research activities and responsibilities
    - ORNL: Laser, plasma, chemical surface modification, mechanical testing, DIC measurements
    - PNNL: Mechanical, plasma, hot gas, transfer film, mechanical testing, environmental testing, surface/interface characterizations
  - Monthly web meetings between research team members
- Adhesives from major adhesive suppliers: Dow Automotive, L&L Product, 3M
- BASF for thermoplastic CFRP and United State Steel for advanced high strength steel

Core Research Team Members

- ORNL: Zhili Feng, Yong Chae Lim, Jian Chen, Monojoy Goswami, Ngoc Nguen, Bradley S. Lokitz, Harry Meyer III, Hui Huang, Wei Zhang, Greg Larsen, Amit Naskar, Yuan Li, Xin Sun
- PNNL: Kevin Simmons, Leo Fifield, Yongsoon Shin, Wenbin Kuang, Gayaneh Petrossian, Daniel Graff, Jonathan Sutter, Matt Prowant

REMAINING CHALLENGES AND BARRIERS

- Adhesive chemistry and additives, compatible to both AHSS and CRFP
- Long-term performance and environmental degradations
- Inhibition of galvanic corrosion
- Compatibility with CTE mismatch
- Scientifically sound, effective approaches to design and engineer high performance adhesives and assembly technologies

REMAINING FUTURE WORK

- Complete in-depth understanding on interface bonding, deformation and roles of adhesive properties and surface engineering at nano/micro scales
  - Connect microscopic behavior to macroscopic level joint deformation and failure
- Surface engineering technology
  - Blown-ion surface modifications on CF-PPA and DP980
  - Detailed chemical analysis of surface modifications and their correlation to mechanical properties
  - Chemical surface modifications and their correlation to mechanical properties.
- Health monitoring of curing/manufacturing process and structural soundness in service

Any proposed future work is subject to change based on funding levels

SUMMARY

- This early stage research focuses on the fundamentals of adhesive bonding of CFRP to AHSS material combination.
- Surface modification techniques, including plasma, silane, and laser treatment, to CFRP (PPA), led to improved adhesive bonding strength
  - Both N2 plasma and silane created preferred chemical group on adherend surface
  - Laser surface treatment modified both surface morphology and surface energy
- A special in-house mechanical test system with m-DIC was developed to provide insights of deformation and failure of bonding interface at microscopic level
  - Revealed strain localization, failure progression, and failure location and mode of the bonding interface
  - Determined critical failure strain values as function of adhesive, surface treatment, adherends, etc …
- Supported a multi-scale adhesive bonding predictive model development
  - Basic property measurement from m-DIC test and coupon level fracture test as input to model prediction
  - Model validation and refinement

TECHNICAL BACKUP SLIDES

APPROACH:
RESEARCH ACTIVITIES IN FY20

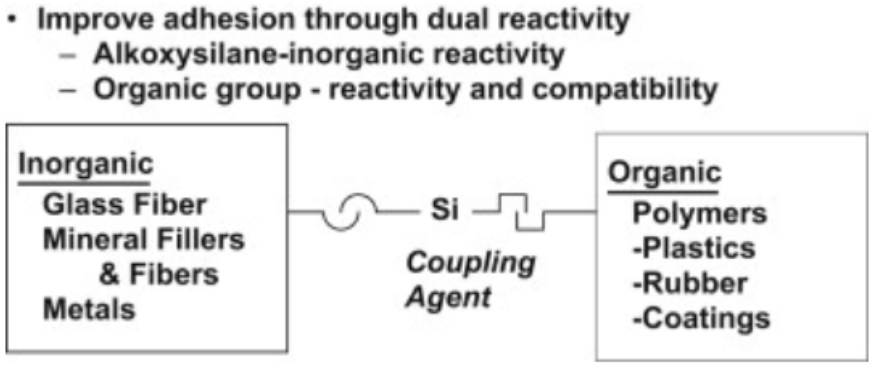
- Activity 1: Surface modifications on adherends (PPA resin only, CFRP (PPA), steel) and characterization
  - Hot gas/plasma treatment: create preferred chemical group on adherend surface
  - Hot press surface with transfer film
  - Chemical surface treatments (dip coat, spray, etc.)
  - Utilize core characterization methods used in this program: water contact angle, laser confocal profilometry, surface chemistry analysis by SEM, FTIR, XPS, TOF-SIMS, etc.
- Activity 2: Evaluation of adhesive bonded specimens with surface modifications
  - Mechanical testing of joints of treated samples (cross tensile pull, DCB, lap shear)
  - Bonding interface characterization (micro-DIC, nano-indentation, TEM, etc.)

ACCOMPLISHMENT AND PROGRESS: SURFACE MODIFICATION OF ADHERENDS BY SILANE

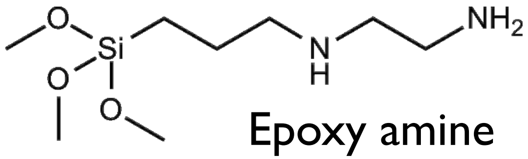
- Chemical surface treatment
  - ➢ Silane coupling agents
  - ➢ Contain functional groups that bond with both organic and inorganic materials
  - ➢ General structure of silane coupling agents

$$R\text{–}Si(OR')_3$$

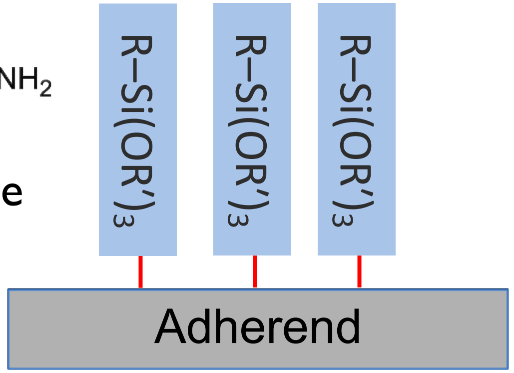
- Where, R is a group that reacts with the liquid adhesive resin
- R’ is usually methyl or ethyl
- ➢ Generally, silane bonds have good durability



Peter G. Pape, in Handbook of Adhesives and Surface Preparation, 2011



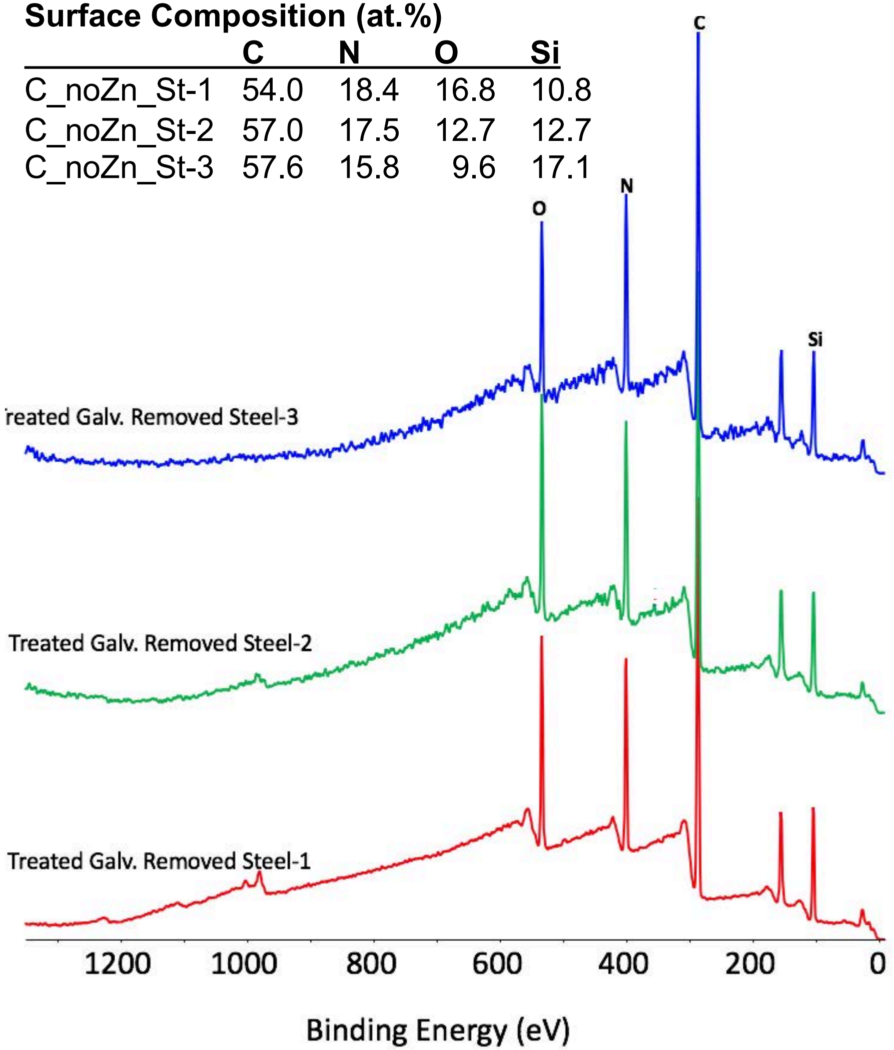
Epoxy amine

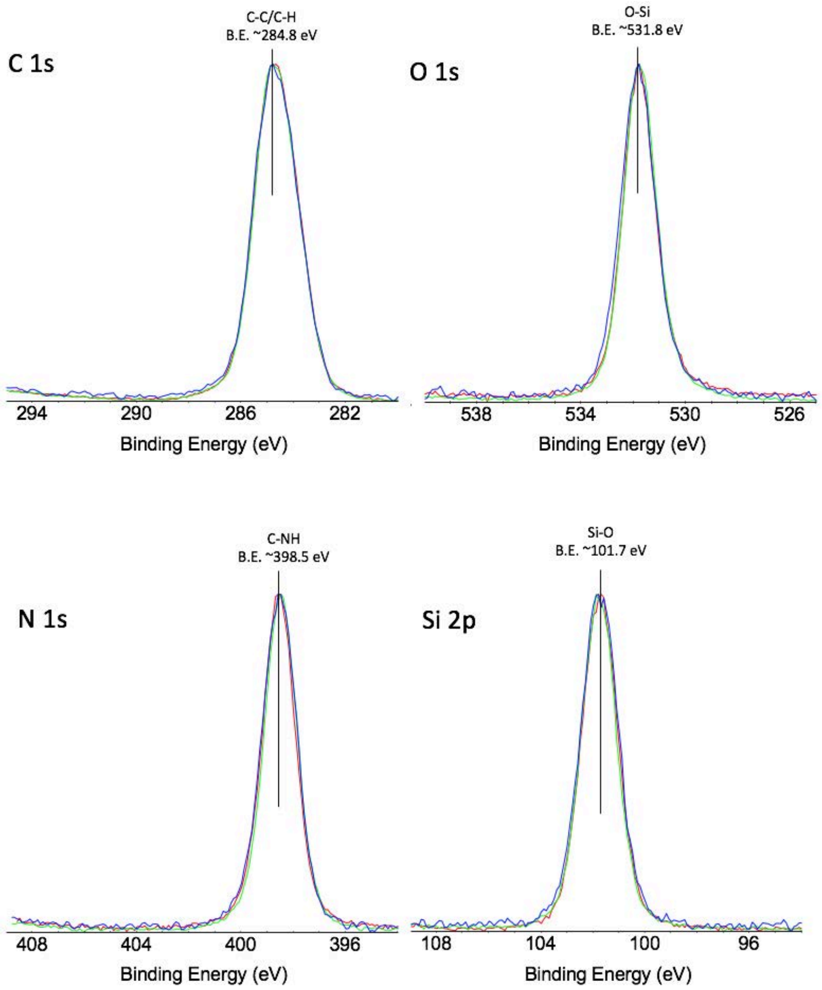


ACCOMPLISHMENT AND PROGRESS: SURFACE CHARACTERIZATION FOR SILANE TREATED STEEL

Surface Composition (at.%)

	C	N	O	Si
C_noZn_St-1	54.0	18.4	16.8	10.8
C_noZn_St-2	57.0	17.5	12.7	12.7
C_noZn_St-3	57.6	15.8	9.6	17.1

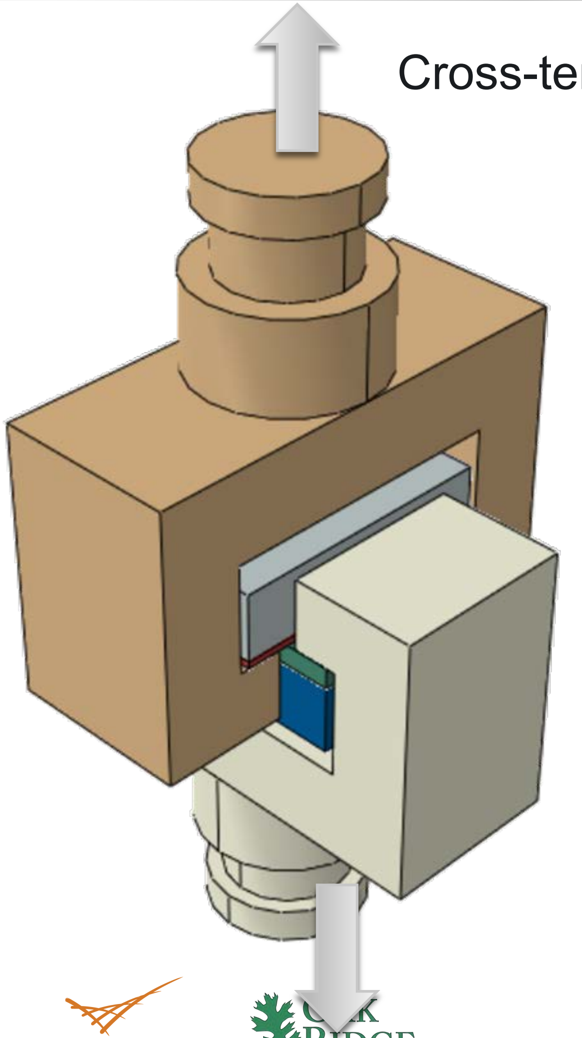




Silane treatment on steel shows similar surface composition compared with silane treated CFRP(PPA)

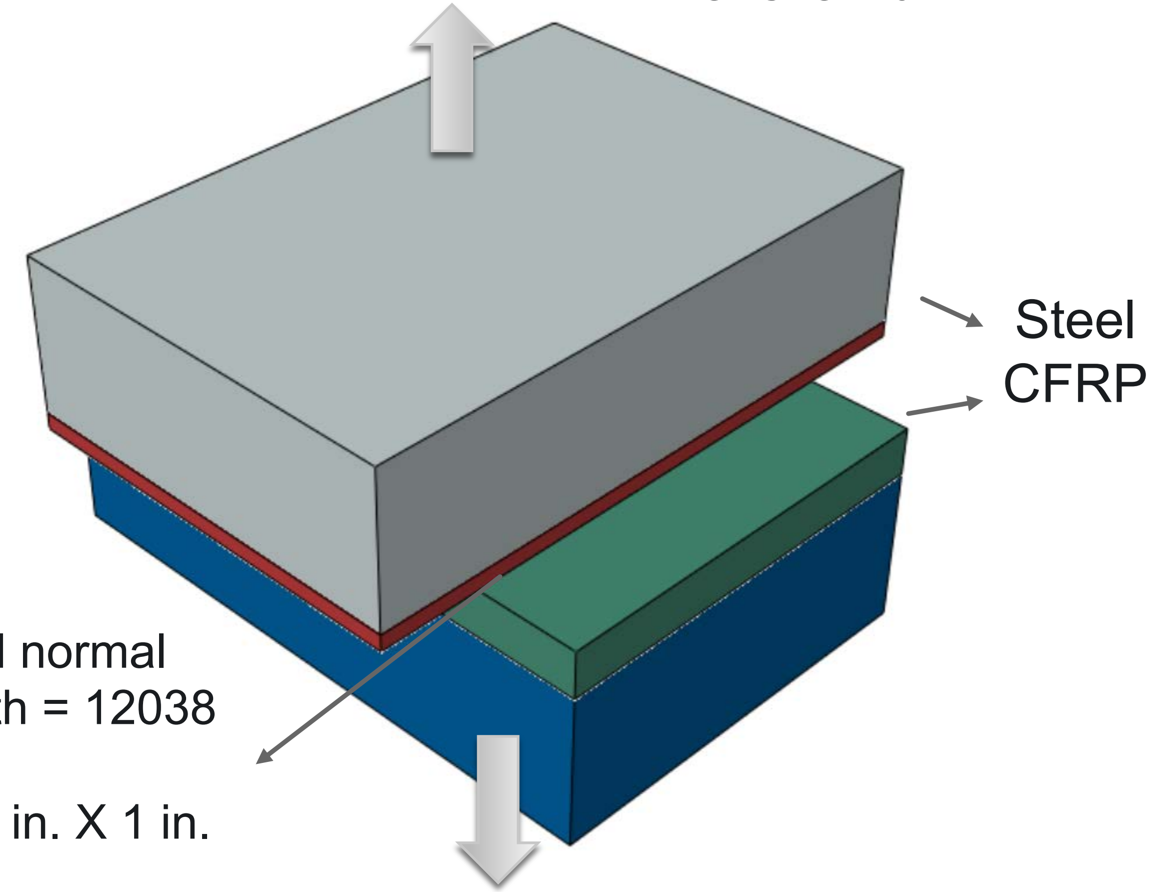
MECHANICAL TESTING
EVALUATION OF TENSION TEST SET UPS FOR ADHESIVE BONDING

Cross-tension test set up



vs

Tensile Pull



Cohesive bond normal interfacial strength = 12038 psi
Bonded area = 1 in. X 1 in.

ACCOMPLISHMENT: μ–DIC SYSTEM